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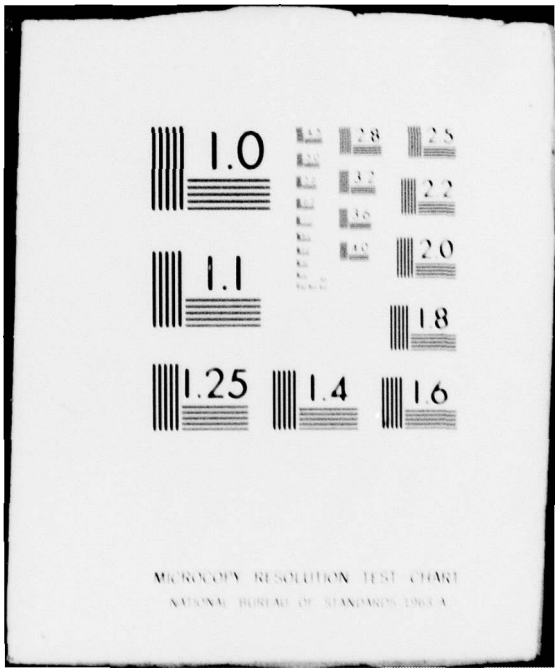
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(10) Ladislav Nemec, Lucille Chia, Hans Jasper Gaehrs and Paul Delahay

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He(I) photoelectron spectra of liquid 1,2-ethanediol were recently obtained by means of two different techniques: (i) irradiation of the liquid film on a rotating disk target and determination of energy distribution curves with a simple retarding potential cell; (ii) use of a liquid jet in conjunction with a conventional 127° analyzer. The liquid-phase spectra obtained by the two techniques are compared and discussed, and the second derivative curve (SDC) for the liquid-phase spectrum obtained by method (i) is compared with the gas-phase spectrum.

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He(I) PHOTOELECTRON SPECTROSCOPY OF 1,2-ETHANEDIOL: COMPARISON OF GAS- AND LIQUID-PHASE SPECTRA

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INTRODUCTION

He(I) photoelectron spectra of liquid 1,2-ethanediol were recently obtained by means of two different techniques: (i) irradiation of the liquid film on a rotating disk target and determination of energy distribution curves with a simple retarding potential cell[1]; (ii) use of a liquid jet (similar to that first described by Siegbahn and coworkers[2]) in conjunction with a conventional 127^{o} analyzer[3]. The He(I) photoelectron spectrum of gaseous 1,2-ethanediol was also reported in Ref. 3. The liquid-phase spectra obtained by the two techniques are compared and discussed in the present note, and the second derivative curve (SDC) for the liquid-phase spectrum of Ref. 1 is compared with the gas-phase spectrum of Ref. 3.

COMPARISON OF LIQUID-PHASE SPECTRA OBTAINED BY TWO TECHNIQUES

Figure 1 shows the spectra from Refs. 1 and 3 normalized to equal quantum yields, that is, to equal areas under each curve. Spectra normalized to equal

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maximum deflection were also compared and led to conclusions identical to those drawn from Fig. 1. The abscissa scales of Fig. 1 were shifted by 0.64 eV to obtain overlapping of the broad shoulder at high T's. The abscissas of the maxima near T = 0 also coincided after this shift. This matter is discussed after comparison of the spectra.

The spectra of Fig. 1 are very similar for $21.2 - T \lesssim 17$ eV, and the first broad band in that region is essentially the same for both spectra. There are, however, two differences at lower kinetic energies: the peak near T = 0 is sharper for Ref. 3 than for Ref. 1, and the shoulder in that region is shifted toward higher T's by ≈ 1 eV for Ref. 1 vs. Ref. 3. Furthermore, the drawn-out curve of Ref. 3 for $21.2 - T > 21.2$ eV is indicative of electron backscattering in the gas phase. These differences can be accounted for by the different vapor pressures (4×10^{-3} torr for Ref. 1 and 50×10^{-3} torr for Ref. 3) at which the two curves were recorded.

The methods by which the kinetic energy scale was calibrated in Refs. 1 and 3 will now be considered. The zero of the kinetic energy scale in Ref. 1 was determined by a modulated capacitance method. A plot was obtained of the capacitance current against retarding potential under the actual operating conditions of the rotating disk target (but without irradiation). The resulting V-shaped curve exhibited a sharp minimum at a retarding potential easily measurable to ± 0.05 V. The minimum capacitance current was practically equal to zero (noise level below 0.05 picoamp). The retarding potential at minimum capacitance current corresponded to zero average field in the gap between the liquid film on the rotating disk and the collector electrode, that is, to T = 0. The retarding potential corresponding to T = 0 varied somewhat

from one liquid to another (up to $\sim$0.5 V). This observation is not surprising if one considers the chain:

metallic rotating disk/liquid/vacuum/metallic collector electrode

In Ref. 3, the stainless steel pipe from which the jet was directed was connected electrically with the walls of the sample chamber and the slit of the energy analyzer. The authors state that "The jet was therefore at the same electrical potential as the slit" (p. 332, lines 8 and 9 of the experimental section). This conclusion is unwarranted and at variance with electrochemical theory and experiment[4]. There is indeed asymmetry between the steel pipe-liquid and liquid-vacuum interfaces. Calibration of liquid-phase spectra with N_2O and Ar applied in Ref. 3 therefore is affected by the uncertainty about contact potentials and so are gas-liquid shifts of spectra. The statement in Ref. 3 that "Agreement with Delahay's spectrum cannot be said to be satisfactory" (p. 338 in Discussion) must be judged in the light of the foregoing comments and the comparison in Fig. 1. The same remark also applies to the difference between threshold values discussed in Ref. 3 (p. 336).

SECOND DERIVATIVE CURVE AND GAS-PHASE SPECTRUM

It was shown in Ref. 5 that the curve (SDC) obtained by differentiation of the energy distribution curve (with respect to kinetic energy) for liquid-phase spectra is an approximate image of the energy spectrum of quasifree electrons upon generation by photoionization in the liquid (case I). The foregoing similarity holds for kinetic energies of emitted electrons below 5 to 10 eV. This limit is very approximate and varies from one liquid

to another. Conversely, at higher kinetic energies (above 10 eV), it is the energy distribution curve which resembles the energy spectrum of electrons[1] (case II). There is a progressive transition from case I to case II, as was shown quantitatively in Ref. 1.

One would expect from the foregoing results that there is a resemblance between the gas-phase spectrum of 1,2-ethanediol and the liquid-phase SDC, at least at sufficiently low kinetic energy of emitted electrons. This is indeed the case (Fig. 2) for $21.2 - T \gtrsim 10$ eV (SDC scale) as case I seems to prevail. The two lowest bands in the gas-phase spectrum are not resolved in the liquid-phase SDC presumably because case II begins to hold. Analogous situations are discussed in Ref. 1. Although the comparison in Fig. 2 is quite striking, it should be mentioned that the SDC analysis involves some assumptions (see Ref. 5) which may be only approximately satisfied in actuality.

The SDC abscissa scale in Fig. 2 was shifted by 1.8 eV to bring about overlapping of similar or related features of the SDC and gas-phase spectrum. The exact value of the shift is tentative, but yields a gas-liquid red shift in the range of those for other liquids reported in Ref. 1.

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CAPTIONS TO FIGURES

Figure 1. Liquid-phase photoelectron spectrum of 1,2-ethanediol according to Ref. 1 (solid curve, lower scale) and Ref. 3 (dashed curve, upper scale). T, kinetic energy of electrons emitted into vacuum.

Figure 2. Second derivative curve (SDC) of liquid 1,2-ethanediol (solid curve, lower scale) from spectrum of Ref. 1 and gas-phase photoelectron spectrum (dashed curve, upper scale) of this substance from Ref. 3.

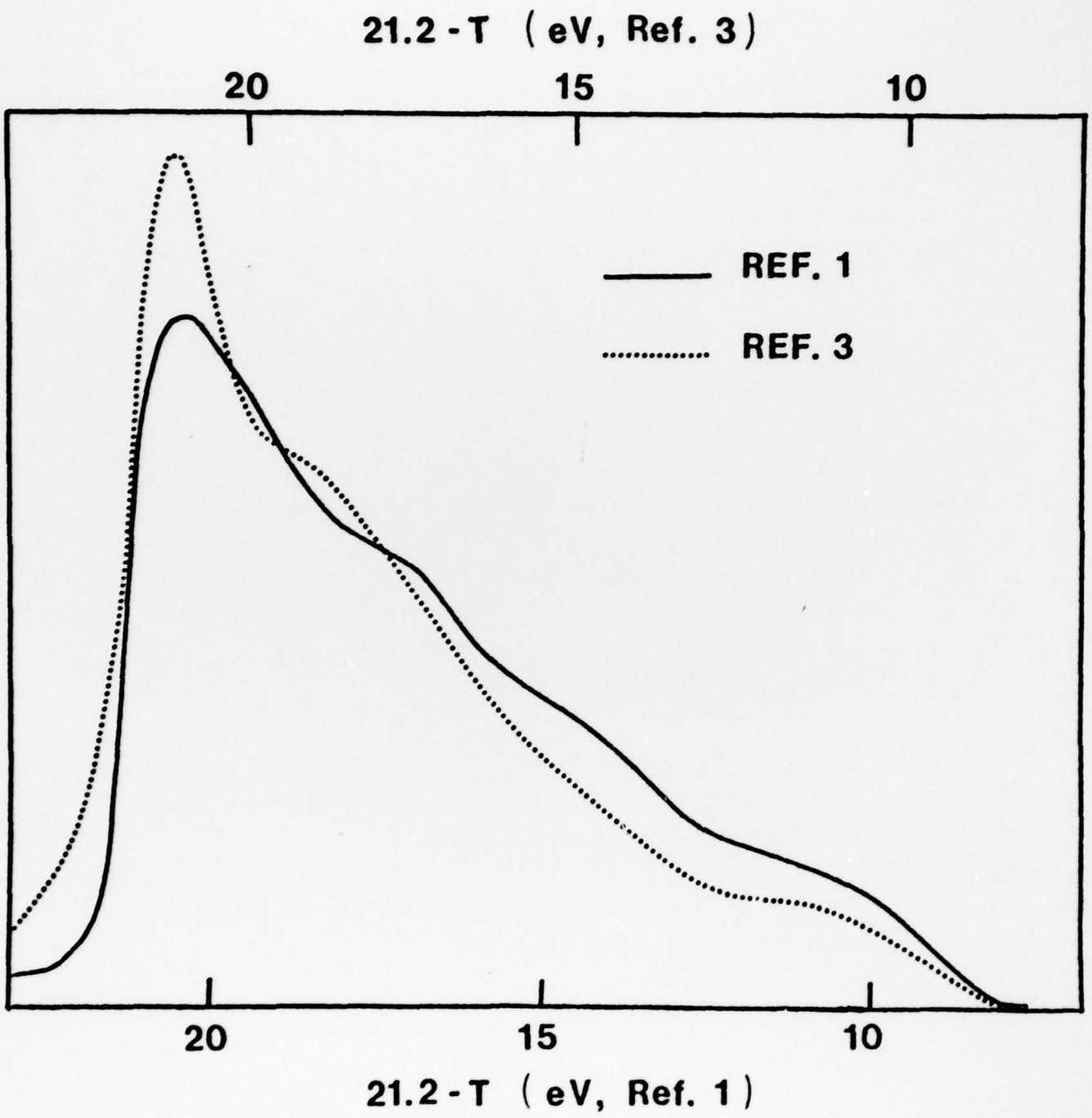
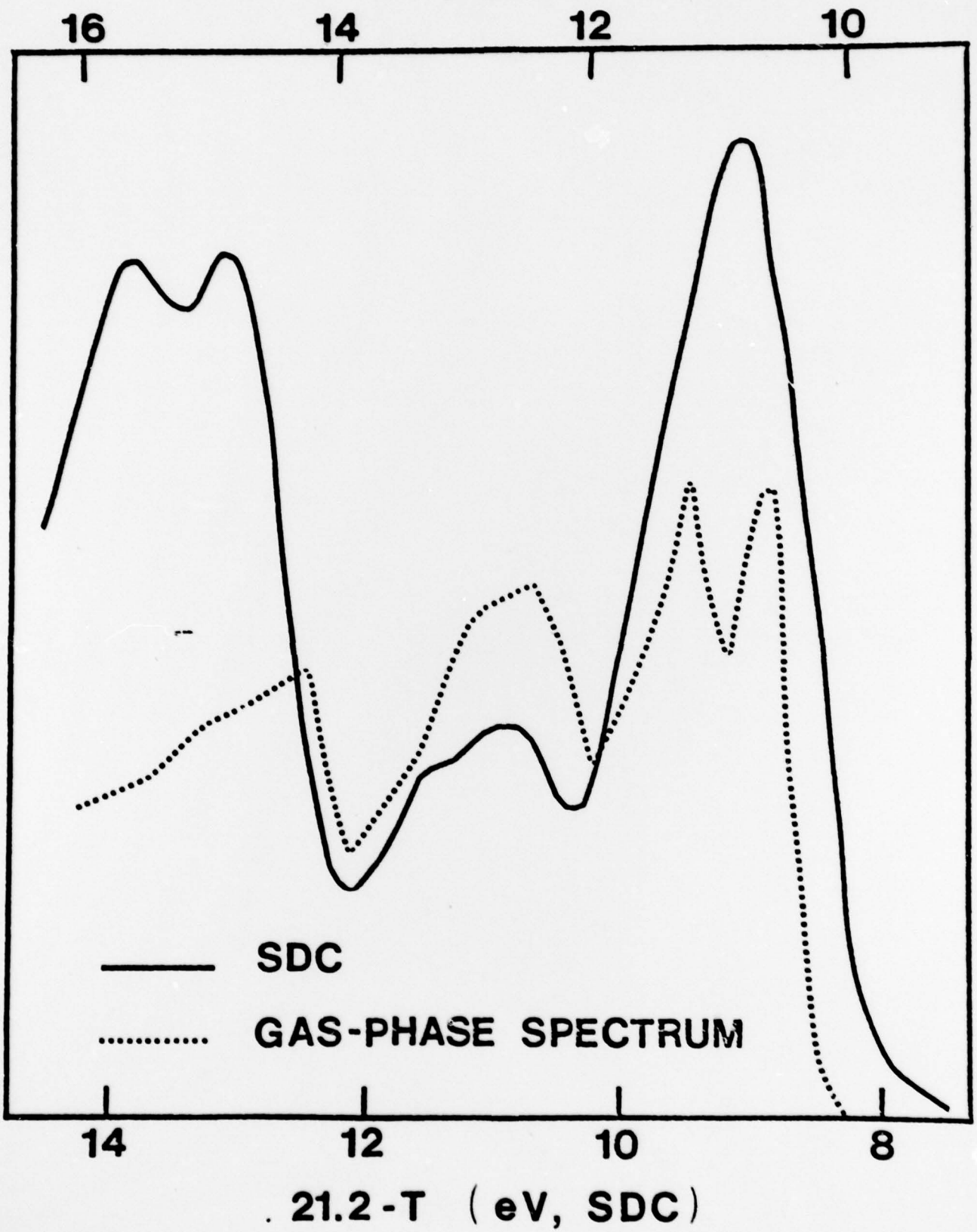


FIGURE 1


21.2 - T (eV, gas phase)
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SDC
GAS-PHASE SPECTRUM
14
12
10
8
21.2 - T (eV, SDC)

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